pH and Photo-responsive Hydrogel Actuators

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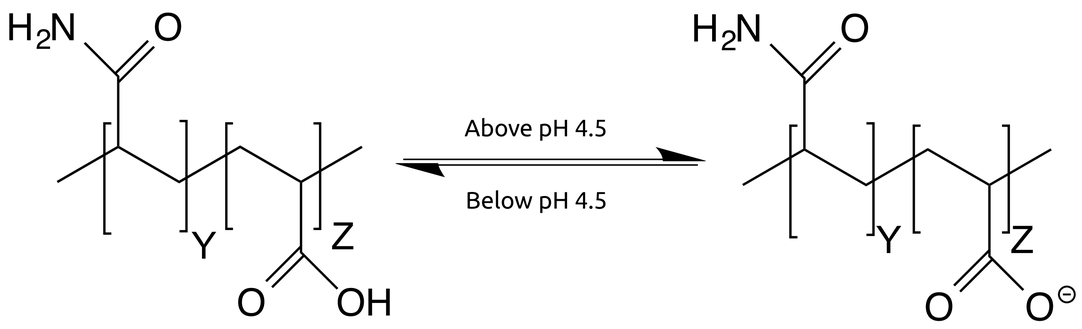
Introduction

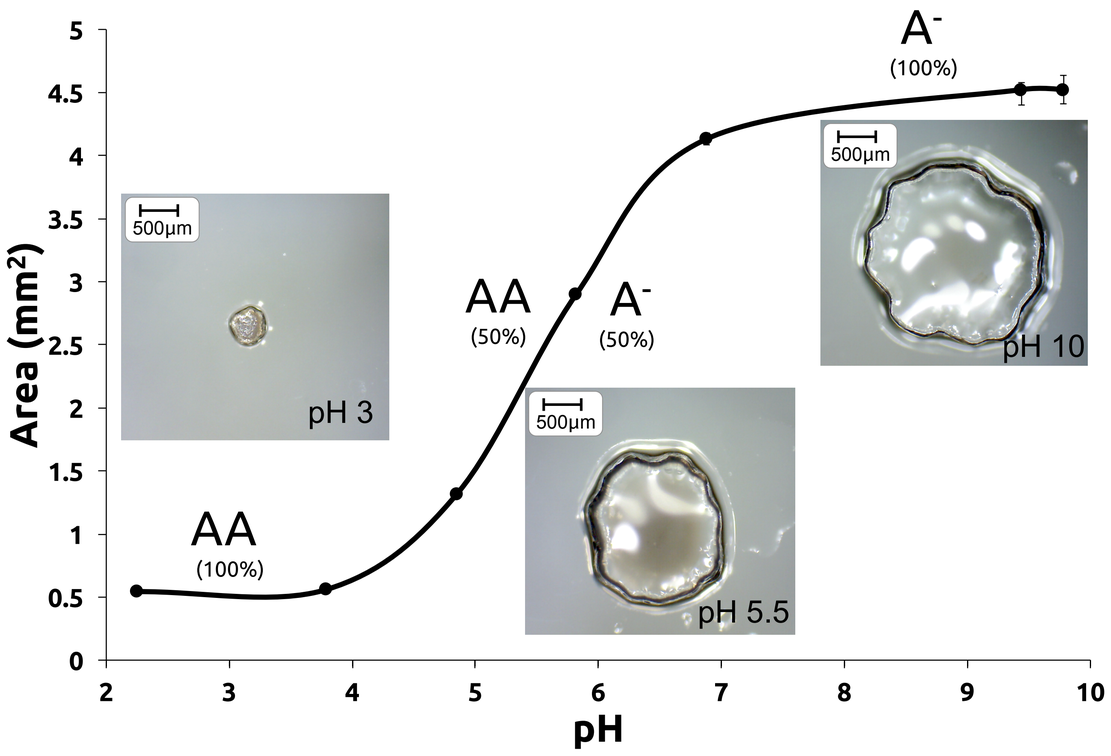
Hydrogels are three-dimensional polymeric networks that can absorb and retain large quantities of water in relation to their physical size. By incorporating stimuli-responsive units into the gel structure, hydrogels can be actuated by external stimuli such as photo, thermal, electro and pH, among others.

In this study, pH responsive hydrogels were developed using copolymers of acrylic acid (AA) and acrylamide (Am) in different molar ratios (30:70, 50:50 and 70:30, respectively).

pH responsive hydrogels



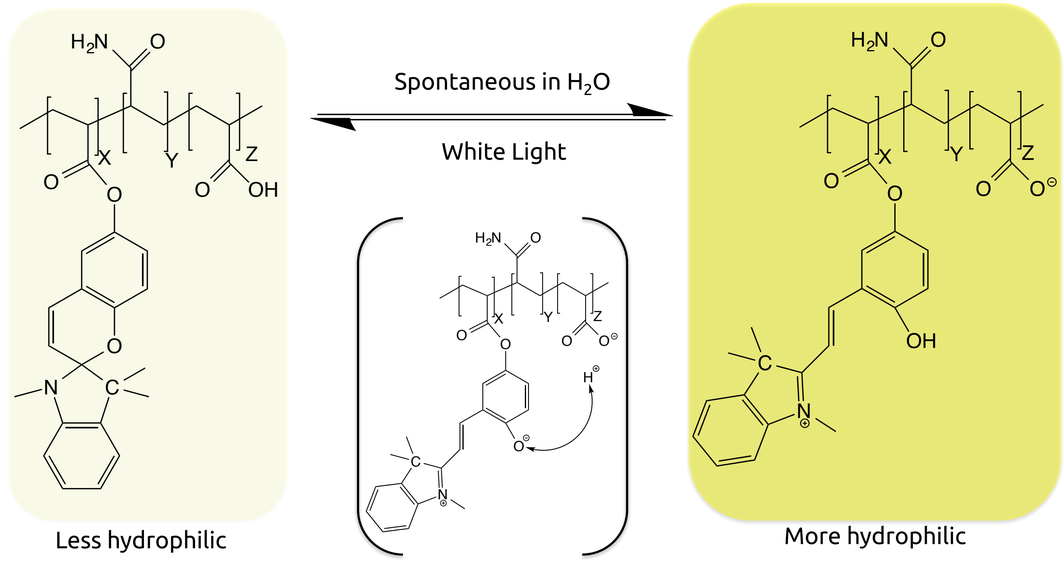
At pH above the pK_a of AA (pK_a~ 4.5) the AA dissociates to the more hydrophilic acrylate (A^-) form triggering swelling of the hydrogel. In contrast, at pH < 4.5, the hydrogel contracts due to the formation of the less hydrophilic AA form in the polymer backbone, which triggers release of water from the gel.



In the case of the 50:50 AAm:AA p(AAm-*co*-AA) circular hydrogels were polymerised that show an area of 0.196 mm^2 at pH 3 compared with 4.52 mm^2 for the same hydrogel at pH 10. This dramatic increase of ~2300% in area is due to the greater amount of hydrophilic acrylate ions being present in the polymer backbone in basic conditions.

From pH to photo-response

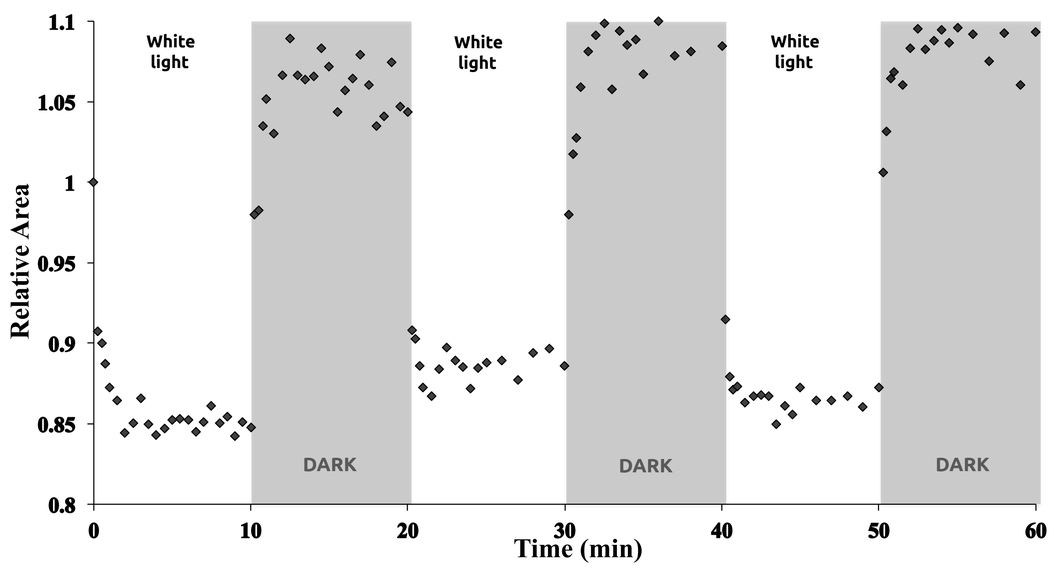
Spiropyran acrylate (SP-A) was copolymerised in the polymer backbone as a photo-acid generator.



When the hydrogel is immersed in water, in the dark, the AA dissociates and the proton is taken by the SP-A to form protonated merocyanine ($MC\text{-}H^+$)(yellow) resulting in hydrogel expansion. When exposed to white light, the $MC\text{-}H^+$ is converted back to SP-A (colourless) and some of A^- gets reprotonated to AA resulting in hydrogel contraction.

Photo-responsive hydrogels

The optimal composition used for the photo-responsive hydrogel was AA: Am: SP-A in a 10:10:1 molar ratio.



The photo-actuation process is reversible, with the initial photo-contraction completed in about 120s and remaining at a constant value as long as the white light is turned ON (10 mins). After the white light is switched OFF the hydrogel reswells to approximately its fully hydrated size in the first 60s in the dark and its size remains relatively constant until the next irradiation cycle. This process was repeated at least 3 times with no detectable hysteresis.

Conclusions

pH responsive hydrogels based on p(AA-Am) have been developed with significant shrinking/swelling capabilities. Introduction of a photo-acid generator, namely SP-A, inside the polymer backbone allowed for reversible hydrogel photo-actuation of over 15% in area in less than 2 minutes.

This project has been funded by Science Foundation Ireland under the Insight initiative, grant SFI/12/RC/2289.